

CHREV. 123

## THE NOMENCLATURE OF CHROMATOGRAPHY

### I. GAS CHROMATOGRAPHY

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#### 1. INTRODUCTION

Today, chromatography is the most widely used and probably also the best documented analytical technique: the number of papers dealing with various aspects of chromatography probably exceeds 100,000. At present, gas chromatography still represents the major chromatographic technique but predictions show that liquid chromatography will surpass it within about 5 years.

The evolution of gas chromatography has a unique characteristic: there has probably not been any other analytical technique where an intensive international cooperation played such a vital role. This cooperation started at the inception of the technique and manifested itself by the frequent meetings, symposia and informal and formal get-togethers in both Europe and the United States.

One of the important subjects of these meetings was the nomenclature of gas chromatography. Discussions on this subject actually started before the first International Symposium held in London in 1956 and represented a major topic there. This discussion was further extended in subsequent years, involving the newly formed Gas Chromatography Discussion Group, an American *ad hoc* Committee and

Committee D-2 of the American Society for Testing and Materials (ASTM)\*. Soon, the British Standards Institution (BS) and the Division of Analytical Chemistry of the International Union of Pure and Applied Chemistry (IUPAC) also became involved in these activities. As a result of this extensive work, three major documents were compiled: the recommendations of the IUPAC first published in 1960<sup>1,2</sup> and then finalized in 1964<sup>3</sup>; the *Glossary of Terms* of BS, first published in 1963 with the presently valid text dated 1969<sup>4</sup>; and the *Gas Chromatography Terms and Relationships* of ASTM E-19, first published in 1968 with the present text approved in 1977<sup>5</sup>. The IUPAC Committee continued its work, expanding it to chromatography in general: the draft of a generalized nomenclature was first published in 1972<sup>6</sup> and finalized in 1973<sup>7</sup>.

The standardization activities were not restricted to nomenclature, terms and symbols only. ASTM in particular has developed three important standards: one dealing in general with gas chromatographic procedures<sup>8</sup> and two dealing with the testing of thermal conductivity<sup>9</sup> and flame-ionization<sup>10</sup> detectors. A similar text on the electron-capture detector was recently completed and will be published later in 1979.

This brief discussion shows that in gas chromatography, well developed, internationally accepted nomenclatures exist. Thus, there is no reason for individuals to invent new symbols and definitions for well established terms. This might be justified in a new field without sufficient international agreements, but certainly not in gas chromatography. Here, individualistic usage is similar to somebody building up his own spelling system, making the reading of publications impossible without a personalized dictionary. We can see examples of this in almost every issue of our scientific and technical journals. Unfortunately, the editors of journals do not prevent this either.

The purpose of this paper is to help to change this situation. It presents these standards, particularly the symbols and key terms specified in them, in detail, and demonstrates their similarities and the few existing differences. We shall deal only with those terms which are in English, although it should be noted that, naturally, standard nomenclatures also exist in other languages. We shall start with a detailed discussion of the evolution of this nomenclature, for two reasons: first, because in general this is necessary in order to understand how the present-day system became established, and secondly, to illustrate that these terms, symbols and definitions are based on extensive cooperation within an international community carried out over more than a decade. After this discussion, we shall deal with the internationally accepted terms and symbols. Finally, we shall discuss the other existing ASTM standards dealing with the specifications of important terms related to the two most frequently used types of gas chromatographic detectors. However, before we start this discussion, two general remarks are necessary.

The first concerns *liquid chromatography*. Although it is the older technique,

\* Committee D-2 on Petroleum Products and Lubricants was the standardization group most closely related to gas chromatography at that time. This is the reason why Research Division IV of this ASTM Committee accepted the original responsibility for this task. These activities were later transferred to ASTM Committee E-19 on Gas Chromatography formed in 1961 which, in 1969, changed its name to Committee on Chromatography, now encompassing all forms of the technique. Naturally, however, the development of standard methods for the analysis of certain samples in which chromatography is used as a method remained the responsibility of the individual ASTM committees.

unification was attempted less in liquid than in gas chromatography. Recently, however, this situation has changed. As already mentioned, the IUPAC Committee accepted a unified chromatographic nomenclature and it also proposed a nomenclature for ion-exchange chromatography and for certain similar techniques; also, at the time of writing this paper, the very detailed nomenclature recommendations of liquid (column) chromatography prepared by ASTM Committee E-19 is being approved, with publication to be expected later in 1979\*. It should be noted that a standardized nomenclature of gel-permeation chromatography developed by ASTM Committee E-20 on Plastics has been in existence since 1972. It is planned to extend the present discussion to the field of liquid chromatography in a later publication.

The second remark is specifically related to the names of certain terms which sometimes are called outdated by certain "innovators". Nobody questions that there is some validity in these remarks; however, the situation is not dissimilar to many other segments of life. After all, almost everything, from spelling to national boundaries, has undergone a historical evolution and the same is also true of terms, definitions and symbols. In this evolution, they often lose their original meaning, but this fact, in itself, does not warrant discarding them. After all, we are still speaking about "chromatography" although (except maybe in TLC) our analyses no longer have anything to do with "color writing". Also, nobody questions that terms, names and definitions originally adopted over 20 years ago, based on a somewhat limited knowledge, might be formulated differently today. For example, if our nomenclature were to be compiled now from scratch, we would probably find better expressions than "adjusted retention time" or "capacity ratio". After all, the former is not "adjusted" but represents the actual retention by the stationary phase and the latter really does not describe the "capacity" of a column (*i.e.*, the amount of sample that can be introduced while still remaining in the linear range). Still, these terms, names and definitions were developed historically and used in thousands of publications, together with the corresponding symbols which were also logically developed, in the context of the whole nomenclature, and, what is even more important, well understood. Thus, there is no real justification to disregard them and create one's own system. Or shall we change the name of America to something else because today, we know that Amerigo Vespucci really became only through a misunderstanding the patron saint, giving his first name to the New World?

## 2. THE EVOLUTION OF GAS CHROMATOGRAPHIC NOMENCLATURE

### *A. The activities of various ad-hoc committees*

As already mentioned, our present-day chromatographic nomenclature is the result of a historical evolution, involving various groups, with members from many countries, and intensive discussions among them. The nomenclature discussion actually started before the 1956 London Symposium and then there a Committee consisting of D. H. Desty, E. Glueckauf, A. T. James, A. I. M. Keulemans, A. J. P. Martin

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\* *Liquid Chromatography Terms and Relationships*, ASTM E 682-79 had been approved on March 30, 1979 by the Membership of Committee E-19 and published recently in Vol. 42 of the 1979 *ASTM Books of Standards* (American Society for Testing and Materials, Philadelphia, Pa., 1979).

and C. G. S. Phillips was formed to formulate some recommendations. In their report<sup>11</sup> they recommended the use of *retention volumes* and established the term which we call today the *specific retention volume* ( $V_g$ ):

$$V_g = \frac{V_N}{W_L} \cdot \frac{273.15}{T_c} \quad (1)$$

*i.e.*, the net retention volume per gram of liquid phase, reduced to 0°C\*. They also specified the *compressibility (pressure drop) correction factor* (calling it then the "reducing factor"), already included in the original 1952 publication of James and Martin<sup>12</sup>, and the *number of theoretical plates* calculated on the basis of the peak width at base obtained by drawing tangents to the points of inflexion of the peak. In this report, the number of theoretical plates was considered as an expression of "column resolution", but the change of this term to *column efficiency* was recommended one year later, by the *ad hoc* Committee of Nomenclature formed at the 1957 Lansing (U.S.A.) Symposium and consisting of W. L. Jones (Chairman), S. Dal Nogare, D. H. Desty, M. J. E. Golay, A. I. M. Keulemans, A. J. P. Martin, S. Ober, C. S. G. Phillips, J. Thoburn and E. Williams<sup>13</sup>. This Committee also established the term *separation factor*,  $\alpha$ , to express the relative position of two adjacent peaks:

$$\alpha = t'_{R2}/t'_{R1} \quad (2)$$

At the 1958 Amsterdam Symposium, a Committee consisting of A. J. P. Martin (Chairman), D. Ambrose, W. W. Brandt, A. I. M. Keulemans, R. Kieselbach, C. S. G. Phillips and F. H. Stross<sup>14</sup> also endorsed the change to "column efficiency" and established a separate *peak resolution* term to express the separation of two adjacent peaks as the distance between the two peak maxima divided by the mean peak width at base:

$$R_s = \frac{t_{R2} - t_{R1}}{\bar{w}_b} = \frac{2(t_{R2} - t_{R1})}{w_{b1} + w_{b2}} \quad (3)$$

It should be noted that a similar term\*\*:

$$R_s = \frac{t_{R2} - t_{R1}}{w_{b1}} \quad (3a)$$

has already been mentioned in the report of the Lansing Committee<sup>13</sup>, as a proposal of M. J. E. Golay, to express resolution. The two expressions are identical if we assume that  $w_{b1} = \bar{w}$ , in other words, that the base width of the *first* peak is identical with the mean base width of the two peaks. For some reason, not the first but the *second* base width was later accepted by convention as assumed to be equal to the mean peak width at base; thus, eqn. 3 was simplified to

$$R_s = \frac{t_{R2} - t_{R1}}{w_{b2}} \quad (3b)$$

This duality can also be seen in the evolution of ASTM E-355<sup>5</sup> concerning the term

\* The symbols used in the text of this report correspond to those recommended by ASTM; see Table 1.

\*\* In the Lansing proposal<sup>13</sup>, no symbol was used for this term; the symbol  $R_s$  is used here for the sake of simplicity.

number of theoretical plates required ( $n_{\text{req}}$ ), to result in a given resolution of peaks 1 and 2 ( $t_{R2} > t_{R1}$ ). This term is expressed by different equations depending on whether we assume eqn. 3a or 3b. If we assume eqn. 3a, the expression for  $n_{\text{req}}$  is

$$n_{\text{req}} = 16R_s^2 \left( \frac{1}{\alpha - 1} \right)^2 \left( \frac{k_1 + 1}{k_1} \right)^2 \quad (4a)$$

and the equation included in the original 1969 text of E-355 (although looking somewhat different) was derived along this line. On the other hand, if we assume eqn. 3b, then the expression for  $n_{\text{req}}$  becomes

$$n_{\text{req}} = 16R_s^2 \left( \frac{\alpha}{\alpha - 1} \right)^2 \left( \frac{k_2 + 1}{k_2} \right)^2 \quad (4b)$$

and this is the equation included in the 1977 version of E-355.

### B. Papers on nomenclature

According to the report of the 1958 Amsterdam Committee, they discussed in detail the contents of two manuscripts, those of Ambrose, Keulemans and Purnell and of Johnson and Stross, to be published in *Analytical Chemistry* and, as a result of this discussion, the authors agreed to certain alterations in order to bring "their recommendations, symbols and nomenclature into line". These two papers were published in the October 1958 issue of the journal; the first<sup>15</sup> was actually prepared at the request of the Committee of the Gas Chromatography Discussion Group, while the second<sup>16</sup> represented the conclusion of the activities of a working group appointed by Research Division IV of ASTM Committee D-2 on Petroleum Products and Lubricants. A third paper by Jones and Kieselbach<sup>17</sup>, published in the same issue of *Analytical Chemistry*, proposed a few additional basic terms: of these, however, only the *average linear carrier gas velocity* became universally accepted.

Almost simultaneously, *Nature* published an important paper by M. J. E. Golay<sup>18</sup> on *Gas Chromatographic Terms and Definitions*, which also addressed itself to the problem of the proper terms. As pointed out by the author, his discussions with workers in the field of gas chromatography convinced him that "much clarification remains to be achieved in nomenclature and definitions of terms" and that particularly two cases create some confusion: the ambiguity of plate number and the HETP for cases when the retention time is not large compared with the gas hold-up time (in other words, for open-tubular columns where the capacity ratio is relatively small), and the resolving power of a column derived from the number of theoretical plates (or HETP).

Concerning the number of theoretical plates, Golay pointed out that for cases when the capacity ratio is not too large, the equation\*

$$n_0 = 5.545 \cdot \frac{t_R t'_R}{w_h^2} \quad (5a)$$

should be preferred to the usual

$$n = 16 \left( \frac{t_R}{w_b} \right)^2 = 5.545 \left( \frac{t_R}{w_h} \right)^2 \quad (5b)$$

\* This expression had already been given by Golay in his paper presented at the American Chemical Society Symposium in Dallas, Texas, in 1956 and published in 1957<sup>19</sup>.

relationship advocated in other publications and also in Keulemans' basic textbook<sup>20</sup>. It should be pointed out that while this expression did not replace the well-established theoretical plate expression (eqn. 5b), it certainly is closer to reality than the so-called *number of effective plates* advocated recently by a number of workers in the field of open-tubular columns.

The second question to which Golay addressed himself in his paper is the "resolving power of a column". He pointed out that in the efficiency of a column the  $t'_R/w_h$  term, which is the inverse of the "relative band width", has an important role. It is interesting to note that Golay's

$$\frac{t'_R}{w_h} = \left( \frac{k}{k+1} \right) \frac{t_R}{w_h} \quad (6)$$

equation, if properly modified (raising to the second power and multiplying each side by 5.545), yields the well known relationship between the number of theoretical plates ( $n$ ) and the number of effective plates ( $N$ ):

$$N = \left( \frac{k}{k+1} \right)^2 n \quad (7)$$

derived later in the literature.

Golay's plate number expression (cf. eqn. 5a), like his *performance index*<sup>21</sup>, was not generally accepted: however, just like the others, this paper also contributed significantly to our understanding of the various relationships that make a column "better".

### C. The activities of the IUPAC committees

Except for Golay's, most of the early nomenclatures expressed retention primarily with respect to volume rather than time, although the corresponding time terms were also mentioned. For some time, there was some confusion concerning the names and symbols of the following terms (using present-day nomenclature and symbols):

the *retention volume* ( $V_R$ ), measured from start;

the *gas hold-up volume* ( $V_M$ ), corresponding to the retention volume of an unretained peak;

the *adjusted retention volume* ( $V'_R$ ), measured from the unretained peak:

$$V'_R = V_R - V_M \quad (8)$$

the *corrected retention volume* ( $V_R^c$ ), representing the retention volume multiplied by the compressibility correction factor ( $j$ ):

$$V_R^c = V_R j \quad (9)$$

the *net retention volume* ( $V_N$ ), representing the adjusted retention volume multiplied by the compressibility correction factor:

$$V_N = V'_R j = (V_R - V_M) j \quad (10)$$

This confusion even exists in the three papers published in the October 1958 issue of *Analytical Chemistry* already cited, and e.g., Ambrose, Keulemans and Purnell<sup>15</sup> admit that some of their symbols are against "general opinion and usage". It was thus clear that the original intention of the discussion at Amsterdam

to eliminate the inconsistencies was not fully accomplished. Therefore, Ambrose and Stross, the Chairmen of the two groups, approached the Analytical Chemistry Division of IUPAC to set up a special group consisting of people from both groups, which would then issue recommendations for a standard terminology in gas chromatography. This group, consisting of D. Ambrose (Chairman), A. T. James, A. I. M. Keulemans, E. Kováts, H. Röck, C. Rouit and F. H. Stross, was duly formed and published the preliminary text of their recommendations in 1960<sup>1,2</sup>. This nomenclature unequivocally established the meaning of certain symbols, adjectives and superscripts. Thus the prime ('), as in  $V'_R$  and  $t'_R$ , and the adjective "adjusted" (*adjusted retention volume and time*) have the meaning that the measurement was made from the unretained peak, while the superscript °, such as in  $V_R^\circ$  and  $t_R^\circ$ , and the adjective "corrected" (*corrected retention volume and time*) indicate that the compressibility correction factor was applied. In *net retention volume (and time)* both superscripts should be used simultaneously; however, because this would be unduly cumbersome, a new symbol,  $V_N$ , was accepted. This recommendation also lists the *specific retention volume* ( $V'_g$ ) and the *number of theoretical plates* ( $n$ ), and the terms related to two peaks: *peak resolution* ( $R_s$ ) and *relative retention* ( $r_{12}$ ), the last representing a generalized form of the *separation factor*, component 2 always referring to the standard.

The preliminary recommendations, originally completed in July 1959 and published in 1960, were finalized as the standard terminology of IUPAC in 1964<sup>3</sup>. In the period 1959–64 the composition of the Committee changed slightly: H. Röck and C. Rouit resigned and were replaced by E. Bayer and, in a consulting capacity, P. Chovin. There are two basic differences between the preliminary and the final text. The first is the introduction of a new term,  $V_g^\ominus$ : this is equal to the net retention volume divided by the amount of liquid phase at column temperature; from eqn. 1 it can be expressed as

$$V_g^\ominus = \frac{V_N}{W_L} = \frac{V_g T_c}{273.15} \quad (11)$$

We should mention that this term did not become accepted in general usage and it is no longer included in the generalized chromatographic nomenclature of IUPAC<sup>6,7</sup>.

The second difference is related to the presentation of data. This subject has been discussed in considerable detail in every committee report since 1956 and various ways and standard components have been suggested. The preliminary recommendations<sup>1,2</sup> still recommended listing the specific retention volume or the partition coefficient, or relative retention data based on certain standards, and eight substances were given as preferred standards. This was changed, however, in the final text: the list of preferred standards was deleted and it was noted that the *retention index system* of Kováts<sup>22</sup> or the *theoretical nonane units* of Evans and Smith<sup>23</sup> are preferred.

\* It should be mentioned that corrected and net retention times have no real physical meaning because one does not apply pressure correction to time. These terms are listed in the ASTM nomenclature<sup>8</sup> simply to represent all of the possible expressions, accepting the definition that retention volumes are obtained by multiplying the respective retention times by the flow-rate. The more correct definition would be that retention volumes are obtained by multiplying the respective retention times by the flow-rate and, if necessary, by the compressibility correction factor. Thus, only three retention times,  $t_M$ ,  $t_R$  and  $t'_R$ , have real physical meaning.

Since 1964, the Commission on Nomenclature of the Division of Analytical Chemistry of IUPAC has been engaged in producing a unified nomenclature applicable to all forms of separation processes. As part of this activity, a Committee consisting of D. Ambrose, E. Bayer and O. Samuelson also considered the possibility of preparing a unified nomenclature encompassing all forms of chromatography. The preliminary recommendations were first published in 1972<sup>6</sup>, then approved in a slightly modified form in 1973 and published in 1974<sup>7</sup>. The major part of these recommendations consists of definitions describing the various terms related to classifications, the separation process, methods, techniques, the visual record obtained and the apparatus used. The differences from the earlier gas chromatographic nomenclature are minor and mostly represent additions of new terms. There are, however, two basic differences compared with both the former IUPAC GC nomenclature and all other nomenclatures: these are related to the partition coefficient and the capacity ratio.

In the case of the *partition coefficient*, the new nomenclature recognized its general use in the literature and thus, while proposing to change its name to "distribution constant" it still retains its symbol although now with the subscript  $D$  ( $K_D$ ). At the same time, however, the new nomenclature introduces a number of other *distribution coefficient* terms and proposes to use the symbol  $D$  (with various subscripts) for them (see later, in Table 2). In the opinion of this author, while the names might be accepted, the symbols should not be because  $D$  has been universally established for the *diffusion coefficient* in gas and liquid phases ( $D_G$  and  $D_L$ , respectively). Concerning the *capacity ratio*, in the new nomenclature it is proposed to change its name to the "mass distribution ratio" and its symbol to  $D_m$ . Again, while the name-change might be accepted, the new symbol has the same problem as mentioned above: it is too similar to the symbol for the diffusion coefficient in the gas phase (for which a number of authors use  $m$  subscript for the *mobile phase*).

#### *D. Nomenclatures of the standardization groups*

The work of the early Committee was continued by the two major English-speaking standardization groups, the British Standards Institution (BS) and the American Society for Testing and Materials (ASTM). The *Glossary of Terms* of the former was first published in 1963 and the presently valid text is dated 1969<sup>4</sup>. As mentioned, early work by ASTM on setting up a consistent and logical system started in Committee D-2 on Petroleum Products and Lubricants, and was continued in Committee E-19 on Gas Chromatography established in 1961, which, in 1969, changed its name to the Committee on Chromatography. The compilation *Gas Chromatography Terms and Relationships* was completed in the second part of 1967 and approved on March 26th, 1968; it was modified in 1977<sup>5</sup>, eliminating some inconsistencies and considering the terms of the generalized IUPAC nomenclature.

### 3. COMPARISON OF NOMENCLATURE RECOMMENDATIONS

#### *A. Symbols*

Table 1 compares the symbols used by BS<sup>4</sup>, ASTM<sup>5</sup>, IUPAC GC<sup>3</sup> and IUPAC generalized<sup>7</sup> nomenclatures. It is evident that all four are almost identical: the only possible misunderstanding could arise with  $V_s$ , which is the solid (active solid



and/or support) volume in the column in the BS and the volume of the stationary phase in the generalized IUPAC nomenclature. It is true that the subscript *S* would be better suited to express the *stationary* phase and the ASTM nomenclature on liquid chromatography now being finalized is considering this; however, in GC, the term *liquid phase* is so well established that there is no reason to change it.

TABLE I  
GAS CHROMATOGRAPHIC SYMBOLS AND TERMS

Parameter	BS	ASTM	IUPAC*	Notes**
Capacity (partition) ratio; capacity factor; mass distribution ratio	$K'$	$k$	$D_m$	See Note 1
Column				
Length	$L$	$L$		
Inside diameter		$d_c$		
Average diameter of solid particles in column		$d_p$		
Average liquid phase film thickness		$d_f$		
Interparticle porosity		$\epsilon$	$\epsilon_1$	See Note 2
Phase ratio	$\beta$	$\beta$		See Note 3 $\beta = V_G/V_L$
Volume of mobile phase in column (interstitial volume)	$V_G$	$V_G$	$V_G, V_I$	See Note 4
Dead volume			$V_d$	See Note 5
Solid volume in column	$V_S$			See Note 6
Specific permeability		$B_s$		
Height equivalent to one effective plate (HEETP)	HEETP	$H$	$H$	
Height equivalent to one theoretical plate (HETP)	HETP	$h$	$h$	
Liquid phase				
Density	$\rho_L$	$\rho_L$	$\rho_L$	
Volume	$V_L$	$V_L$	$V_L, V_S$	See Note 7
Weight (mass)	$w_L$	$W_L$	$w_L$	
Mobile phase (volumetric) flow-rate				
At column outlet and ambient temperature		$F_u$	$F$	
Same as above but corrected to dry gas conditions		$F_c$		$F_c = F_u \cdot \frac{P_a - P_w}{P_w}$
At column outlet corrected to column temperature	$F_c$	$F_c$	$F_c$	See Note 8
Mobile phase (interstitial) velocity				
At column outlet		$u_c$	$u_c$	
Average in column	$\bar{u}$	$\bar{u}$	$\bar{u}$	$\bar{u} = L/t_M = u_c \cdot i$
Optimum average		$\bar{u}_{opt}$		
Mobile phase viscosity		$\eta$		
Number of effective plates	$N$	$N$	$N$	See Note 9 $N = 16(t'_R/w_b)^2$ $= 5.545(t'_R/w_b)^2$
Number of theoretical plates	$n$	$n$	$n$	$n = 16(t_R/w_b)^2$ $= 5.545(t_R/w_b)^2$

(Continued on p. 244)

TABLE 1 (continued)

Parameter	BS	ASTM	IUPAC*	Notes**
Number of effective plates required for a given resolution of peaks 1 and 2		$N_{req}$		$N_{req} = 16R_s^2 \left( \frac{\alpha}{\alpha - 1} \right)^2$ $= n_{req} \left( \frac{k_2}{k_2 + 1} \right)^2$ See Note 10
Number of theoretical plates required for a given resolution of peaks 1 and 2		$n_{req}$		$n_{req} = 16R_s^2 \left( \frac{\alpha}{\alpha - 1} \right)^2 \left( \frac{k_2 + 1}{k_2} \right)^2$ See Note 10
Partial pressure of water at ambient temperature		$P_w$	$p_w$	
Partition coefficient (distribution constant)	$K$	$K$	$K, K_D$	See Note 11
Peak resolution	$R$	$R_s$	$R_s$	$R_s = \frac{2(t_{R2} - t_{R1})}{w_{b1} + w_{b2}}$
Peak width				
At base		$w_b$		See Note 12
At half-height		$w_h$		See Note 12
At inflexion points		$w_i$		
Pressure				
Column inlet	$p_i$	$P_i$	$p_i$	
Column outlet	$p_o$	$P_o$	$p_o$	
Column, relative		$P$		$P = P_i/P_o$
Factor relating pressure drop and column permeability		$j'$		$j' = \frac{3}{4} \cdot \frac{P^2 + 2P + 1}{P^2 + P + 1}$
Pressure gradient (compressibility) correction factor	$j$	$j$	$j$	$j = \frac{3}{2} \cdot \frac{P^2 - 1}{P^3 - 1}$
Pressure drop		$\Delta p$		$\Delta p = P_i - P_o$
Ambient		$P_o$	$p$	
Retention index	—	$I$	$I$	No symbol is given in BS system
Relative retention	$r_{12}$	$r_{1s}$	$r_{12}$	See Note 13
Retention times			$t_{A,B}$	
(Gas) hold-up time	$t_M$	$t_M$	$t_M$	
Retention time	$t_R$	$t_R$	$t_R$	From start
Adjusted retention time	$t'_R$	$t'_R$	$t'_R$	$t'_R = t_R - t_M$
Corrected retention time		$t''_R$		
Net retention time		$t_N$		
Retention volumes				
Gas hold-up volume	$V_M$	$V_M$	$V_M$	$V_M = t_M F_c$
Corrected gas hold-up volume		$V'_M$		$V'_M = V_M j$
Retention volume (total retention volume)	$V_R$	$V_R$	$V_R$	See Note 14 $V_R = t_R F_c$
Adjusted retention volume	$V'_R$	$V'_R$	$V'_R$	$V'_R = t'_R F_c = (t_R - t_M) F_c$
Corrected retention volume		$V''_R$	$V''_R$	See Note 15
Net retention volume	$V_N$	$V_N$	$V_N$	$V_N = V'_R j = \frac{t'_R F_c j}{273.15}$
Specific retention volume	$V_g$	$V_g$	$V_g$	$V_g = \frac{V_N}{W_L} = \frac{V_g T_c}{273.15}$
Net retention volume per gram of liquid phase at column temperature			$V_g^\ominus$	$V_g^\ominus = \frac{V_N}{W_L} = \frac{V_g T_c}{273.15}$ See Note 16
Separation factor (relative retention)	$\alpha$	$\alpha$	$\alpha_{A/B}$	Always refers to two adjacent peaks
Temperature (absolute)				
Ambient		$T_a$	$T_m$	
Column	$T$	$T_c$	$T$	

\* If there is any conflict between the two IUPAC nomenclatures (GC and generalized), this is given in a Note.

\*\* In equations the ASTM symbols are always used.

*Notes:*

1. The symbol  $D_m$  is used in the generalized IUPAC nomenclature. The IUPAC GC nomenclature did not include this term.
2. The term "interstitial fraction" is used by IUPAC in both nomenclatures.
3. IUPAC recognizes this term but does not specify any symbol.
4. The IUPAC GC nomenclature is using the symbol  $V_G$  while the generalized chromatography nomenclature is using  $V_I$  (subscript  $I$  for "interstitial").
5. The generalized IUPAC nomenclature defines "dead volume" as *the volume between the effective injection point and the effective detection point, less the column volume*.
6. BS is using this symbol to express the effective volume occupied by the active solid and/or the solid support in the column. IUPAC GC nomenclature specifies this term as *the volume occupied by the solid support or the active solid in the column*, however, without using any specific symbol.
7. The IUPAC GC nomenclature is using the symbol  $V_L$  (subscript  $L$  for "liquid" phase), while the generalized IUPAC chromatography nomenclature is using  $V_S$  (subscript  $S$  for "stationary" phase). There is a conflict between the symbol  $V_S$  used by BS for the *solid volume in the column* and the IUPAC symbol  $V_S$  for *the volume of the stationary phase in the column*.
8. The BS definition is ambiguous: it refers to "column outlet temperature", which may mean either column temperature or ambient temperature. On the other hand, at other points, it is clear that column temperature is considered here.
9. IUPAC, in the generalized nomenclature, calls it the "effective theoretical plate number".
10. In the equations for  $n_{req}$  and  $N_{req}$ ,  $u = t'_{R2}/t'_{R1}$ ;  $k_2 = t'_{R2}/t'_M$  and  $t'_{R2} > t'_{R1}$ .
11. The  $K_D$  symbol is proposed in the generalized IUPAC nomenclature as a compromise between the old  $K$  and the newer proposal for suggesting  $D$  for the *distribution constant*.
12. BS and IUPAC are using the appropriate term without any specific symbol. "Peak width" as such automatically means in both the BS and IUPAC nomenclatures the peak width at base. One should always avoid the term "half-width": it is not half of the width (as one would expect from this expression) but the full width at 50% of the maximum peak height.
13. While the symbol  $\alpha$  always refers to two adjacent peaks, the symbol  $r$  refers to any two peaks in a chromatogram. The difference in the meaning of the subscripts is explained in the text.
14. The expression "total retention volume" is included in the generalized IUPAC nomenclature for further clarification.
15. From the two IUPAC nomenclatures this term exists only in the GC nomenclature.
16. This term exists only in the IUPAC GC nomenclature.

Below, a few remarks are made about the symbols listed in Table 1\*.

(a) First, it should be noted that in all three nomenclatures great care was taken to avoid any ambiguity. Thus, since the subscript  $g$  has already been assigned to the specific retention volume,  $V_g$  ( $g$  for "gram of liquid phase"), the subscript  $G$  is used for the *gas phase*; hence, the equivalent subscripts  $M$  and  $L$  are also used for the mobile and the liquid phase, respectively. Another reason for this decision was the ambiguity that lower case  $l$  can be easily mistaken for the numeral "one". Thus, lower case  $l$  is *never* used, either as a symbol or as a subscript: column length is  $L$  and liquid phase is characterized by the subscript  $L$  and not  $l$ .

Naturally, this rule also means that the same considerations should also be valid for other symbols, *e.g.*, the respective diffusion coefficients in the gas and liquid phases should be  $D_G$  and  $D_L$  and not  $D_g$  and  $D_l$ , as one often finds in publications.

(b) Similarly, as  $r$  represents relative retention, the subscript  $c$  is always used in the symbol for column radius ( $r_c$ ); furthermore,  $r$  should never be used as a sub-

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\* Having served for many years as both a member and the Chairman of the Subcommittee of Nomenclature of ASTM E-19, the author of this review is one of the most authoritative persons to attest to the validity of this explanation.

script: the subscript for "retention" is  $R$ , as in  $t_R$  and  $V_R$ . Similarly, the symbol for "peak resolution" is  $R$  or, even better,  $R_s$ .

(c) All of the other subscripts are lower case letters, such as in  $V_g$ ,  $d_c$  and  $d_f$ .

(d) In the nomenclatures care was taken *never* to use composite symbols consisting of two letters. Thus, proposals for symbols such as  $tm$ ,  $ts$  and  $tms$  are not only against the words but also against the spirit of the official, carefully compiled nomenclatures, irrespective whether lower case or capital letters are used. The only exception is HETP, which, however, is not a "symbol" (the corresponding symbol is  $h$ ) but an acronym.

(e) There is a specific reason why in gas chromatography both the symbols for the gas phase ( $G$ ) and the mobile phase ( $M$ ) are used, although they obviously mean the same:  $G$  refers to the gas volume irrespective of compressibility (*i.e.*, the geometric volume), while  $M$  refers to a *flowing* mobile phase with a higher inlet than outlet pressure, thus automatically considering the compressibility factor. In other words,  $V_G$  is the volume of the gas (mobile) phase in the column under static conditions whereas  $V_M$  is the gas hold-up volume in an analysis and, under ideal conditions (*i.e.*, no extra-column "dead" volume):

$$V_G = V_M j = V_M^{\circ} \quad (12)$$

In fact, the difference ( $V_M^{\circ} - V_G$ ) indicates the extra-column volume of the system.

(f) Note that *all four nomenclatures* are clear in using  $n$  for the number of *theoretical* plates and  $N$  for the number of *effective* plates, and that both ASTM and IUPAC are also clear in using  $h$  and  $H$  for HETP and HEETP, respectively. Thus, there is no excuse for mixing them up, *e.g.*, by using  $N$  for the theoretical plate number. Another clear agreement is in the symbols for velocity:  $u$  or  $\bar{u}$ . One can often find symbols such as  $v$ ,  $w$  or  $\mu$  in the literature, and again, there is no excuse for it. Similarly, there is a clear agreement in using  $\beta$  for the *phase ratio* and  $a$  for the *separation factor*.

(g) The ASTM nomenclature uses  $P$  in general for *pressure* while the others use  $p$ ; also, ASTM uses  $W_L$  for the *weight of liquid phase in the column*, compared with  $w_L$  by the others. There is no possibility of misinterpreting the former and thus this does not represent any problem;  $W_L$  was deliberately selected by ASTM instead of  $w_L$  because the symbol  $w$  generally refers to the *peak width*.

There are two areas where disagreements between the nomenclatures may result in misinterpretation of certain data: these refer to the capacity ratio and certain subscripts referring to specific peaks.

From the very beginning, gas chromatographers were almost equally divided in the symbol for the *capacity ratio*: in the United States,  $k$  has always been used (and  $K$  for the *partition coefficient*), while European scientists used  $k'$  or  $K'$  for the capacity ratio and  $k$  or  $K$  for the partition coefficient. Unfortunately, this discrepancy still exists and one may have equal arguments for either usage.

Finally, a few notes are necessary concerning the *subscripts* used in the symbol for the separation factor and the relative retention, denoting the individual peaks. Here, ASTM is very clear: if the subscripts 1 and 2 are used, then  $t_{R1} < t_{R2}$ , *i.e.*, 2 refers to the peak emerging *later*. Thus, the separation factor as expressed by eqn. 2 in this report is, by definition, always larger than unity. The same is also

true of the generalized IUPAC nomenclature where  $\alpha_{A/B} = K_{D(A)}/K_{D(B)}$  and  $K_{D(A)} > K_{D(B)}$ . On the other hand, in the BS nomenclature, although the symbol is the same and  $\alpha = K_A/K_B$ , the meaning of the subscripts is reversed ( $K_B > K_A$ ). Thus, as interpreted by BS,  $\alpha < 1$  because  $K_A$  is the partition coefficient of the *first* peak.

In the case of relative retention, the *definition* is the same in all four cases: the adjusted retention time, volume or the partition coefficient of the substance of interest divided by the same term for the standard. However, the subscripts are not the same, creating the possibility of confusion. In ASTM, the subscripts of *i* and *s* are used for the peak of interest and the standard, respectively; on the other hand, both BS and the IUPAC GC nomenclature use *1* for the peak of interest and *2* for the standard, and the generalized IUPAC nomenclature uses *A* for the substance of interest and *B* for the standard.

Finally, a few recommendations included only in the ASTM nomenclature should be mentioned, such as  $d_f$  for the *average liquid phase film thickness* in open-tubular columns,  $d_c$  for the *inside column diameter* (and hence, logically,  $r_c$  for the *inside column radius*) and  $B_c$  for the *specific column permeability*. Particularly the last-mentioned symbol is noteworthy: one may find in the literature about as many symbols for this term as there are publications!

### B. Terms and definitions

As already mentioned, all these nomenclatures also include definitions of various terms. Table 2 lists these terms (except those already included in Table 1) for which clear definitions are given in these nomenclatures. It is interesting to quote the definition of chromatography from the generalized IUPAC nomenclature:

A method used primarily for separation of the components of a sample, in which the components are distributed between two phases, one of which is stationary while the other moves. The stationary phase may be a solid, or a liquid supported on a solid, or a gel. The stationary phase may be packed in a *column*, spread as a *layer*, or distributed as a *film*, etc.: in these definitions *chromatographic bed* is used as a general term to denote any of the different forms in which the stationary phase may be used. The mobile phase may be gaseous or liquid.

As there is practically no ambiguity in the definitions given in these standards, they are not discussed individually here, except for one. As can be seen in Table 2, three of the four standards are very clear in defining the columns first described by M. J. E. Golay in 1957 as *open-tube* or *open-tubular* columns and *not* as *capillary* columns. Open-tubular columns are very clearly defined in the standards as

a column containing stationary phase but having an unobstructed axial channel (BS):

(*having*) unobstructed central gasflow channels (ASTM):

a column, usually of capillary dimensions, in which the column wall, a liquid or an active solid supported on the column wall acts as the stationary phase (IUPAC).

As can be seen, "capillary" is simply given as an indication of the usual diameter but not as a characterization of the column type. This is even clearer in the BS nomenclature where, in addition to "open-tubular columns", we also find a separate definition for "capillary columns":

A column of capillary dimensions, generally less than 1 mm internal diameter.

TABLE 2  
TERMS (OTHER THAN THOSE IN TABLE 1) WHICH ARE DEFINED IN THE STANDARD NOMENCLATURES

<i>Term</i>	<i>BS</i>	<i>ASTM</i>	<i>IUPAC GC</i>	<i>IUPAC* general</i>	<i>Notes**</i>
Absolute detector	+				
Active solid	+	+	+	+	
Adsorption chromatography				+	
Adsorption column	+				
Air peak			+		
Auxiliary gas	+				
Backflush	+				
Baseline	+	+	+	+	
Bypass injector	+	+	+	+	
Capillary column	+				
Carrier gas	+	+	+	+	See Note 1
Chromatogram	+	+	+	+	
Chromatograph (verb)				+	
Chromatograph (noun)				+	
Chromatography				+	
Column	+	+	+	+	
Column chromatography				+	
Column packing		+			
Column performance (= number of theoretical plates)			+	+	
Concentration distribution ratio, $D_c$				+	See Note 2
Concentration-sensitive detector	+				
Conditioning	+				
Detection				+	
Detector	+	+	+	+	
Differential chromatogram				+	
Differential detector	+		+	+	
Differential (concentration) detector		+			
Differential (mass) detector		+			
Distribution coefficients					
$D_o$				+	See Note 3
$D_r$				+	See Note 3
$D_s$				+	See Note 3
Displacement chromatography				+	
Dynamic range	+				
Dynamic range, linear	+				
Dynamic ratio	+				
Effluent	+			+	
Eluate				+	
Eluent				+	
Elute (verb)				+	
Elution band				+	See Note 4
Elution chromatography				+	
Final temperature				+	
Flow-programmed chromatography				+	
Frontal chromatography				+	
Fronting	+				
Gas chromatograph	+				

(Continued on p. 249)

TABLE 2 (continued)

<i>Term</i>	<i>BS</i>	<i>ASTM</i>	<i>IUPAC GC</i>	<i>IUPAC* generai</i>	<i>Notes**</i>
Gas chromatography (GC)	+	+	+	+	
Gas-liquid chromatography (GLC)	+	+	+	+	
Gas-solid chromatography (GSC)	+	+	+	+	
Gas-displacement chromatography		+			
Gas-elution chromatography		+			
Gas-frontal chromatography		+			
Initial temperature				+	
Injection point				+	
Injection temperature				+	
Integral chromatogram				+	
Integral detector	+	+	+	+	
Integrator	+				
Internal standard	+		+	+	
Isothermal gas chromatography				+	
Linear dynamic range	+				
Liquid phase	+	+	+		
Liquid phase loading		+			
Liquid volume			+		See Note 5
Marker	+			+	
Mass distribution ratio, $D_m$				+	See Note 6
Mass-sensitive detector	+				
Mobile phase	+		+	+	
Modified active solid				+	
Modified sorbent	+				
Normalization	+				
Open-tube chromatography				+	
Open-tube (open-tubular) column	+	+		+	
Partition chromatography				+	
Packed column	+	+		+	
Packing	+			+	
Partition column	+				
Peak	+	+	+	+	
Peak area	+	+	+	+	
Peak base	+	+	+	+	
Peak height	+		+	+	
Peak maximum	+			+	
Peak integration	+				
Porous-layer open-tube (PLOT) column		+			
Programmed-flow gas chromatography	+	+			
Programmed-pressure gas chromatography	+				
Programmed-temperature gas chromatography (PTGC)	+	+			
Pyrolysis-gas chromatography		+			
Reaction-gas chromatography		+			
Relative response factor	+				
Response	+				
Response factor	+				
Retention temperature				+	
Sample injector	+		+	+	

(Continued on p. 250)

TABLE 2 (continued)

Term	BS	ASTM	IUPAC GC	IUPAC* general	Notes**
Sample inlet system		+			
Separation temperature				+	See also retention temperature
Solid, active	+	+			
Solid support	+	+	+	+	
Solid volume			+		See Note 7
Solvent (liquid phase)		+	+		
Solute		+	+		
Stationary phase	+	+	+	+	
Step	+	+	+	+	
Step height	+	+	+	+	
Support, solid	+	+	+	+	
Support-coated open-tube (SCOT) column		+			
Tailing	+			+	
Temperature-programmed chromatography				+	
Traps		+			
Unresolved peak				+	
Unretained substance		+			
Wall-coated open-tube (WCOT) column		+			
Zone				+	

\* Those terms which refer only to chromatographic methods other than gas chromatography are not listed here.

\*\* Notes:

1. In GC, this term is used for "eluent" or the "mobile phase".
2. The concentration distribution ratio:

$$D_c = \frac{\text{amount of component in stationary phase per cm}^3 \text{ of stationary phase}}{\text{amount of component in mobile phase per cm}^3 \text{ of mobile phase}}$$

is a generalized name for the partition coefficient, now called distribution constant, for which the symbol  $K_D$  is also permitted.

3. The generalized IUPAC nomenclature recognizes three distribution coefficients:

$$D_g = \frac{\text{amount of component in stationary phase per gram of dry stationary phase}}{\text{amount of component in mobile phase per cm}^3 \text{ of mobile phase}}$$

$$D_v = \frac{\text{amount of component in stationary phase per cm}^3 \text{ of bed volume}}{\text{amount of component in mobile phase per cm}^3 \text{ of mobile phase}}$$

$$D_s = \frac{\text{amount of component adsorbed per m}^2 \text{ of surface}}{\text{amount of component in mobile phase per cm}^3 \text{ of mobile phase}}$$

Of these,  $D_g$  is applicable in ion-exchange and gel chromatography, where swelling occurs, and in adsorption chromatography with adsorbents of unknown surface area;  $D_v$  is applicable when it is not practicable to determine the weight of the solid phase;  $D_s$  is applicable in adsorption chromatography with a well characterized adsorbent of known surface area.

4. Synonymous with "peak".
5. Defined as the volume of the liquid phase in the column.



## 6. The term

$$\frac{\text{amount of component in stationary phase}}{\text{amount of component in mobile phase}}$$

existing in all four expressions ( $D_c$ ,  $D_g$ ,  $D_v$  and  $D_s$ ) is called the *mass distribution ratio* ( $D_m$ ) instead of *capacity factor* or *capacity ratio* (see Table 1).

## 7. Defined as the volume of the support or active solid in the column.

This clear distinction between the two terms is very important, as not every open-tubular column is a capillary column and not every capillary column is an open-tubular column! Without making this clear distinction, we might create confusion, particularly in liquid chromatography where recently both open-tubular columns of capillary dimensions and packed capillary columns have been described for improving column efficiency.

Recently, interest in open-tubular columns has greatly increased and we even find biannual international symposia dealing with advances in this field and, in the name of these symposia, the expression "capillary column" is used. This is, of course, against all the accepted international nomenclatures.

## 4. OTHER GAS CHROMATOGRAPHY STANDARDS

ASTM has also developed four other standards related to gas chromatography as a technique\*. The first is E-260, which specifies the general instrumentation and the information needed to describe a chromatographic method exactly<sup>8</sup>; two others then specify how to test a thermal conductivity<sup>9</sup> and a flame-ionization<sup>10</sup> detector. A standard dealing with the electron-capture detector is in the final approval stage at the writing of this review.

A. *Recommendations on the general procedure*

E-260 had been developed at a relatively early stage of gas chromatography; in fact, the idea of its compilation originated in Committee D-2, before the organization of Committee E-19, and it originally had a specific purpose. It was around 1960 that analytical procedures utilizing gas chromatography started to be developed by a number of ASTM Committees (and, in fact, also by other groups) active in various fields. At that time, it was felt that a detailed recommendation was needed to describe the individual parts of a GC equipment and to specify what represents a proper gas chromatographic system\*\*; to detail the manipulations (*e.g.*, preparation of column packing) an average gas chromatographer must carry out in a routine analytical laboratory; and to enumerate the individual information which should be included and specified in an ASTM "standard method". There is no question that today this standard is outdated in many respects (*e.g.*, of the eight detector types discussed only three have today any importance), and the compilation of a greatly modified text is in progress. For this reason, we shall not deal with these recommendations but will

\* Naturally, there are a large number of ASTM and BS standards in which gas chromatography is used as the analytical method. However, here we deal only with those the subject of which is the technique itself.

\*\* Generally, an ASTM Method also specifies the basic equipment to be used for the given measurement.

mention only that there are still a number of valid points in the existing text, particularly those listing the conditions that one must specify in a GC analytical method.

### B. Terms related to detectors

The two other ASTM standards quoted specify the methods of testing thermal conductivity (TCD) and flame-ionization (FID) detectors. Both describe in detail how to use the exponential dilution flask, permeation tubes or the dynamic method for testing and give definitions of sensitivity, minimum detectability, linear range, response time, noise and drift.

*Noise* is the amplitude expressed in microvolts (TCD) or amperes (FID) of the envelope of the baseline which includes all random variations of the detector signal of a frequency on the order of one or more cycles per minute. As explained, this corresponds to the observed noise: the *actual* noise of the system may be larger or smaller than the observed value, depending on the method of data collection or signal monitoring from the detector.

*Drift* is the average slope of the noise envelope expressed in microvolts (TCD) or amperes (FID) per hour as measured over  $\frac{1}{2}$  h. Fig. 1 illustrates both noise and drift.

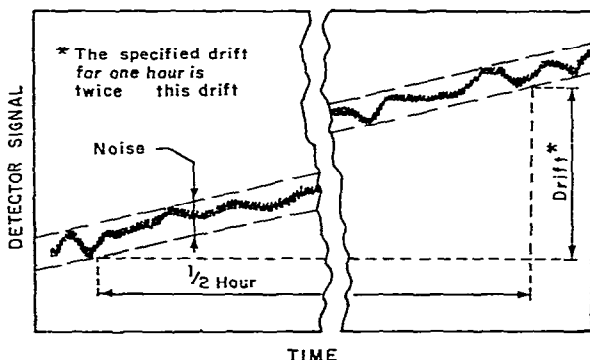


Fig. 1. Example of the measurement of the drift and noise level of GC detectors. From ASTM E 516 and E 594.

*Response time* is primarily important for thermal conductivity detectors. It is the time required for the output signal to reach 63.2% of the new equilibrium value when the composition of the gas entering the detector is changed in a stepwise manner, within the linear range of the detector. The internal volume and geometry of the detector have to be stated in connection with the response time specification. Response time can be determined and specified at various flow-rates. Fig. 2 shows the graphical determination of the response time from the recorder chart obtained in a high-speed recorder\*.

In the case of the flame-ionization detector, response time is not important because the time constant of ionization is negligible and the transit time of the sample

\* This method was first described by Schmauch<sup>24</sup>.

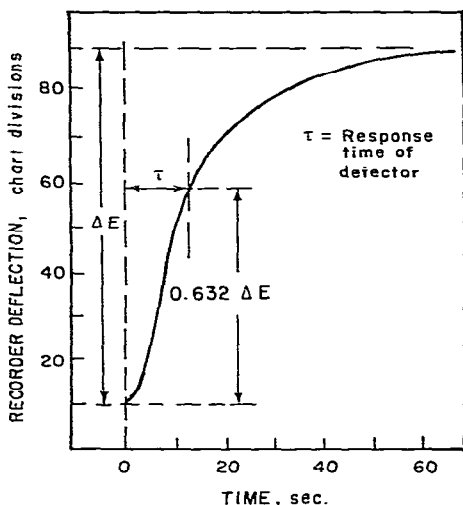


Fig. 2. Example of the measurement of response time of a thermal conductivity detector. From ASTM E 516.

through the detector has little influence. In fact, in a typical FID, not the detector itself, but the electrometer/amplifier is the limiting factor.

The basic expression of *sensitivity* is the same, but in detail it depends on the type of detector, whether it is based on concentration (TCD) or mass flow-rate (FID). Thus, sensitivity is the signal output (peak height) per unit concentration (TCD) (eqn. 13) or unit mass (FID) (eqn. 14) of a test substance in the column effluent:

$$S_{\text{TCD}} = \frac{(P.H.)}{W_s/w_v} = \frac{(P.H.) w_v}{W_s} \quad (13)$$

$$S_{\text{FID}} = \frac{(P.H.)}{W_s/w_t} = \frac{(P.H.) w_t}{W_s} \quad (14)$$

where *P.H.* is the peak height at maximum, in millivolts (TCD) or amperes (FID), and  $W_s$  is the weight of the test substance in the sample, in grams or milligrams; *w* represents the peak width at half-height expressed either as time ( $w_t$ ) (minutes for the TCD and seconds for the FID) or in volume ( $w_v$ ) (in milliliters). The latter can be calculated as

$$w_v = w_t F_c \quad (15)$$

where  $w_t$  is expressed in minutes and  $F_c$ , the flow-rate of the carrier gas corrected to column temperature, in milliliters per minute.

Detector sensitivity can also be calculated from the peak area determined either manually or by electronic integration, but the area value obtained in square centimeters or square millimeters, or counts, must be corrected into the units specified below. In this case,

$$S_{\text{TCD}} = \frac{AF_c}{W_s} \quad (13a)$$

$$S_{\text{FID}} = \frac{A}{W_s} \quad (14a)$$

where  $A$  is the peak area in  $\text{mV} \cdot \text{min}$  (TCD) or  $\text{A} \cdot \text{sec}$  (FID). Thus, the respective dimensions of  $S_{\text{TCD}}$  and  $S_{\text{FID}}$  are  $\text{mV} \cdot \text{min} \cdot \text{g}^{-1}$  or  $\text{A} \cdot \text{sec} \cdot \text{g}^{-1}$ . It should be noted that the sensitivity values calculated from eqn. 13 vs. eqn. 13a and eqn. 14 vs. eqn. 14a will differ by 6%, the difference between peak area calculated using the peak width at half-height and the true peak area.

*Minimum detectability* is the concentration (TCD) or mass flow (FID) of the test substance in the carrier gas that gives a detector signal equal to twice the noise level, and can be calculated from the measured sensitivity and noise level:

$$M.D. = 2(N.L.)/S \quad (16)$$

Here,  $M.D.$  refers to the minimum detectability,  $N.L.$  is the noise level (in millivolts for the TCD and amperes for the FID) and  $S$  is the calculated detector sensitivity, in  $\text{ml} \cdot \text{ml} \cdot \text{g}^{-1}$  (TCD) or  $\text{A} \cdot \text{sec} \cdot \text{g}^{-1}$  (FID).

The *linear range* of a detector can generally be expressed in three ways. In the traditional way, it is shown as log-log plots, plotting peak area (or height) against concentration (in milliliters per minute, for the TCD) or mass flow-rate (in grams per second, for the FID) of the sample in the column effluent. The shortcomings of this presentation are that it is almost impossible to investigate the variation (randomness) within the range\* and the end-point of the range cannot be exactly determined. Therefore, both ASTM standards advocate the presentation of the linear range as the plot of sensitivity\*\* vs. the values representing the amount of sample, *i.e.*, the concentration (in milligrams per milliliter, for the TCD) or the mass flow-rate (in grams per second, for the FID) in the column effluent at the detector. Fig. 3 shows a typical presentation: as can be seen, these are semilogarithmic plots. The linearity plot represents, by specification, the smooth line through the data points. This line must be within  $\pm 5\%$  of the constant value obtained by a least-squares fit of the lower decades (four specified for the FID). At the end of the linear range the plot will curve downwards. The end of the linear range is the point where the plot crosses the  $-5\%$  envelope.

The third way of presenting the linear range is simply to give the ratio of the end of the linear range and the minimum detectable limit. For example, if the respective values are  $1 \cdot 10^{-5}$  and  $4 \cdot 10^{-12}$  g/sec, then the linear range is  $2.5 \cdot 10^6$ . Needless to say, if the linear range is specified in this way, the minimum detectable limit must also be given.

\* Except with help of linear regression analysis, giving the regression coefficient.

\*\* As the sensitivity value for a TCD is directly proportional to  $A/W_s$  (*cf.*, eqn. 14a), one can simply use  $A/W_s$  instead of sensitivity.

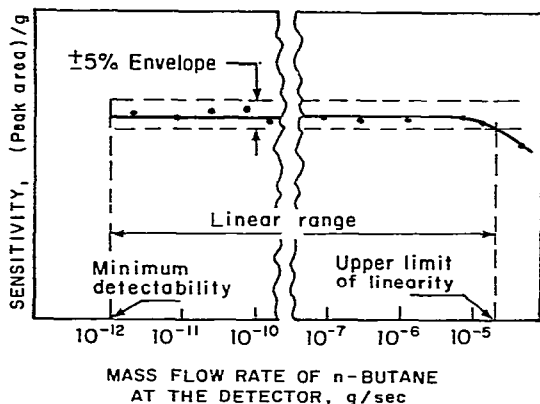


Fig. 3. Example of the linearity plot of a GC detector. From ASTM E 594. The values on the abscissa are typical of a flame-ionization detector. A similar plot would be obtained for a thermal conductivity detector, plotting the concentration of the sample in the column effluent at the detector.

## 5. ACKNOWLEDGEMENT

I express my appreciation to the American Society for Testing and Materials for permitting the reproduction of Figs. 1–3.

## 6. SUMMARY

The nomenclature of gas chromatography is reviewed with special emphasis on its evolution and recommendations by early *ad-hoc* committees which represented the basis of the very detailed nomenclatures developed and published by the British Standards Institute, the American Society for Testing and Materials, and the International Union of Pure and Applied Chemistry. The terms and symbols included in the existing four standards (BS 3282; ASTM E 355-77; IUPAC GC and general chromatography nomenclatures) are compared and some additional existing rules outlined. Finally, other existing standards related to gas chromatography as a technique are also discussed.

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